**Synthesis and Characterization of 4-Thiazolidinones based on 4-amino-N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)benzenesulfonyamide**

The Chapter-2 deals with the synthesis and characterization of Schiff bases (anils, azo methines or imines) of 4-amino-N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)benzenesulfonyamide. The presence of >C=N- group is of great importance by considering the fact that it can be transformed into various heterocyclic ring compounds. The availability of the presence and significant biological properties of the members known so far prompted the authors to extend moieties like 2-azetidinones, 4-thiazolidinones, 2-pyrrolidinones and pyrrole-2-ones. In this context, the present chapter deals with the synthesis and characterization of 4-thiazolidinones. The whole chapter is divided into two parts. The brief reviews about the 4-thiazolidinones have been summarized in **PART-I** and the experimental part are summarized into **PART-II**.
PART-I

Brief reviews about the 4-thiazolidinones

4.1 Thiazolidinones

Thiazolidinones (tetrahydrothiazole) [1,2] are synthesized by the condensation of β-aminomercaptans with aldehydes or ketones and may also be prepared by reducing 2-thiazolines with aluminum amalgam [3]. Their stability varies, but their behavior indicates a general tendency to regenerate the components of syntheses, with which indeed they may exist in equilibria [4] (XXIX).

Thus with mercuric chloride they yield the appropriate mercaptides and with oxidizing agents (I₂, Br₂, H₂O₂) yield oxidation products (disulphides or sulphonic acids) derived from the mercaptants. N-acylation greatly increases ring stability as is known by oxidation of these acyl derivatives to cyclic sulphoxides and sulphones.

4.2 4-Thiazolidinones

The 4-carbonyl derivative of thiazolidine is known as 4-thiazolidinone (XXX).
4.2.1 Synthetic methods for the preparation of 4-thiazolidinones

4-thiazolidinones are prepared by the various methods.

- By the interaction
  
  (a) Of thioglycolic acid, or its ester, and Schiff bases [5-7].
  
  (b) Of mercaptoacetamide and aldehydes in presence of dehydrating agent [8].

\[
\text{COOH} \quad \text{SH} \quad \text{N} \quad \text{Ph} \quad \text{Ph} \quad \text{N} \quad \text{Ph}\n\]

\[
\text{O} \quad \text{N} \quad \text{Ph} \quad \text{Ph} \quad \text{S}\n\]

(XXXI)

More known compounds prepared are 2-phenyl-4-thiazolidinone (XXXII), m.p. 128\(^0\)C; 3-methyl-2-phenyl-4-thiazolidinone (XXXIII), b.p. 147-149\(^0\)C; 3-ethyl-2-phenyl-4-thiazolidinone(XXXIV), m.p. 55\(^0\)C; 2,3-diphenyl-4-thiazolidinone (XXXV), m.p. 132\(^0\)C.

- 2-(5'-carboxypentyl)-4-thiazolidinone (octithiazic acid) (XXXVI), m.p. 139-140\(^0\)C

It was isolated from culture broths of a strain of streptomyces and synthesized through the resolved brucine salt, from mercaptoacetamide and pimelaldehyde ester (OHC-(CH\(_2\))\(_3\)-COOMe) exhibits in vitro activity against mycobacterium tuberculosis.
• 2-imino-4-thiazolidinone (XXXVII) (Pseudothiohydentoin), dec. 250\(^0\)C.

It was obtained from thiourea and ethyl chloroacetate or chloroacetic acid [9], the latter method being adaptable to include hydrolysis to 2,4-diketothiazolidine [10] (XXXVIII), m.p. 129\(^0\)C.

By consideration with benzaldehyde the parent compounds afford 5-benzylidene-2-imino-4-thiazolidinone, dec. 280-290\(^0\)C (XXXIX) and 5-benzylidene-2,4-thiazolidinedione (XL), m.p. 240\(^0\)C respectively. The former may be hydrogenated to 5-benzyl-2-imino-4-thiazolidinone, m.p. 218\(^0\)C [11] and the accessibility of the 5-arylidene-diones combined with their easy hydrolysis by alkali to thioglycolic acid, Ar-CH\(_2\)-CS-COOH (of rhodamines) indicates their potential value for synthetic work.

• 2-imino-5-hydroxyisopropyl-4-thiazolidinone chars at 200\(^0\)C.
Prepared from methyl dimethylglycidate, and thiourea, is dehydrated by acetic acid forming 2-amino-5-isopropylidene-4-thiazolidinone (XLI) and hence by hydrolysis with sulphuric acid 5-isopropylidene-4-thiazolidinedione (m.p. 166°C) also produced by heating isopropylidene-rhodamine with lead acetate aqueous ethanol. Similar condensation of ethyl phenylglycidate and thiourea affords 5-benzylidene-2-imino-4-thiazolidinone which like benzylidene rhodamine reacts with aniline forming 2-anilino-5-benzylidene-4-thiazolidinone [12], m.p. 250°C.

- 2-imino-3-phenyl-4-thiazolidinone (XLII) (m.p. 218°C)
  
  It is prepared from chloroacetanilide and potassium thiocyanate, yields 3-phenyl-thiazolidine-2,4-dione (XLIII) on hydrolysis, but is unstable and undergoes thermal rearrangement to 2-anilino-4-thiazolidinone (dec. 203°C) which is hydrolyzed to a mixture of 2,4-thiazolidinedione and its 3-phenyl derivative [13,14].
4.2.2 Biologically active 4-thiazolidinone derivatives

In order to determine the effect of substitution in the 5\textsuperscript{th}-position of thiazolidinone nucleus, 3-(3-butilaminopropyl)-5-ethyl-2-phenyl-4-thiazolidinone hydrochloride have been prepared by Alaxander [15]. The structure is shown below (XLIV).

![Image of formula XLIV](image)

where, R= H and R’= alkyl, cycloalkyl, etc.

Hassan and co-workers [16] synthesized various 10-(p-substituted arylidene sulphanilyl) phenothiazines by condensation of 10-sulphanilyl phenothiazine with substituted aromatic aldehydes. Interaction of Schiff bases with mercaptoacetic acid afforded 10-(p-thiazolidinonyl benzene sulphonyl) phenothiazines (XLV).

![Image of formula XLV](image)

where, Ar= Ph, furfuryl, p-OCH\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}, etc.
N.C. Desai et al [18] have synthesized some 2-aryl-3-isonicotamido-4-thiazolidinone derivatives (XLVI) as potential antitubercular and antibacterial agents.

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{H} & \quad \text{N} \\
\text{R} & \quad \text{O} \\
\text{ZnCl}_2 & \quad \text{SHCH}_2\text{COOH} \\
\end{align*}
\]

(XLVI)

where, R = 3-Cl-C\text{6}H\text{4}, 4-CH=C\text{6}H\text{4}, etc.

A.J. Baxi et al [19] have prepared a series of 3-(3’-carboxyphenyl sulphonamido)-2-aryl-5H-4-thiazolidinone (XLVII) by condensation route and were screened for their antimicrobial activity.

\[
\begin{align*}
\text{COOH} & \quad \text{O} \\
\text{Ar} & \quad \text{S} \\
\text{N} & \quad \text{N} \\
\text{S} & \quad \text{O} \\
\end{align*}
\]

(XLVII)

where, Ar = Ph, CH=CH-C\text{6}H\text{5}, etc.

Bhagwat and coworkers [20] have synthesized some thiazolidinone derivatives bearing 2,4-bithiazol moiety (XLVIII).
S.K.Srivastava and R.B.Pathak [21] have synthesized ether containing thiazolidinone compounds with a view to screen their antifungal activity having the below general structure (XLIX).

\[
\text{(XLIX)}
\]

where, \( R = R' = \text{H, Me, Cl, etc.} \)

V.H.Joshi et al [22] have synthesized new 4-thiazolidinones (L) and screened them for antitumor and antitubercular activities.
where, $R = \text{Ph, 2-Cl-C}_6\text{H}_4$, etc.

R.S.Lodhi and co-workers [23] have reported several 2-(substituted aryl)-3-(N$^1$-imidazolyl acetamidyl)-4-oxo thiazolidines (LI) and they were tested for their biological activity.

where, $R$ and $R’ = \text{aryl, substituted aryl}$.

S.K.Srivastava et al [24] have synthesized various 5-arylidene-2-aryl-3-(2-chloro phenothiazino acetamidyl)-1,3(H)-thiazolidin-4-ones as an antifungal and anticonvulsant agents (LII).
where, $\text{Ar} = \begin{array}{l}
\text{Ar}^\prime = 2\text{-Cl-}C_6H_4, 3\text{-Cl-}C_6H_4, \text{etc.} \\
R = \text{H, Cl, Me, etc.}
\end{array}$

R.C.Sharma and Devendrakumar [25] have synthesized new 4-thiazolidinones (LIII) and are evaluated for their antimicrobial activities.

\[
\begin{array}{c}
\text{O}_2\text{N} & \text{N}
\end{array}
\begin{array}{c}
\text{Ar}
\end{array}
\begin{array}{c}
\text{S}
\end{array}
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\]  

(LIII)

where, $\text{Ar} = \text{pyridyl, benzthiazolyl, etc.}$

S.K.Srivastava and co-workers [26] have synthesized some thiazolidinone derivatives (LIV) containing carbazole group. They are found to be antifungal and analgesic agents.

\[
\begin{array}{c}
\text{N}
\end{array}
\begin{array}{c}
\text{H}
\end{array}
\begin{array}{c}
\text{Ar}
\end{array}
\begin{array}{c}
\text{Ar}'
\end{array}
\begin{array}{c}
\text{S}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\]  

(LIV)

where, $\text{Ar} = \text{Ar}^\prime = 4\text{-NO}_2\text{-}C_6H_5, \text{etc.}$
Soumya srivastava and co-workers [27] indicated, 5-arylidene-2-aryl-3-(1,2,4-triazoloacetamidyl)-4-thiazolidinone (LV) as antibacterial, antifungal, analgesic and diuretic agents.

![Chemical structure of LV](image)

where, Ar= 2-Cl-C₆H₄, 3-Cl-C₆H₄, etc.

H.S.Joshi et al [28] have synthesized some 4-thiazolidinones (LVI) bearing benzo[b]thiophene nucleus as potential antitubercular and antimicrobial agents.

![Chemical structure of LVI](image)

where, R= 3-Br-C₆H₄, 3-Cl-C₆H₄, etc.

Reda M Fikry et al [29] have synthesized 4-thiazolidinones from 2-aminothiazoles containing coumarin moiety. The general structure is as below (LVII).
where, Ar= C\textsubscript{6}H\textsubscript{5}, 4-OCH\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}, etc.

El’tsov O. S. et al \cite{30} prepared (imidazolylimino)-thiazolidinones (LVIII) and (LIX).

where, Ph= aromatic aldehydes.

Synthesis of N-substituted-3-aminothiazolidin-4-ones containing heteroaryl fragments was carried out by Kelarev V. I. \cite{31} (LX), (LXI) and (LXII).
PART-II

SYNTHESIS AND CHARACTERIZATION OF
4-THIAZOLIDINONES DERIVATIVES

4.3 Experimental

Various Schiff bases Schiff based of 4-amino-N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)benzene sulfonamide (6a-h) mentioned in chapter-2 on heterocyclization reaction with mercapto acetic acid yield the biologically active 4-thiazolidinones (8 a-h). These derivatives were characterized by elemental analysis, Infrared spectroscopy and Proton magnetic resonance. The research work is scanned in Scheme 4.1.

Experimental procedure for synthesis of this series of compounds has been adopted according to reported method [32, 33].

4.3.1 Materials

The Schiff bases (6a-h) have been selected for the synthesis of above said compounds. Their synthesis has already been described in Chapter-2. Other chemicals used were of LR grade.
4.3.2 Synthesis of N-(4-(2,4-dichlorophenyl)-6-(6-methyl
naphthalen-2-yl)pyrimidin-2-yl)-4-(4-oxo-2-phenyl
thiazolidin-3-yl)benzenesulfonamide (8a-h).

A mixture of Schiff bases (6a-h) (0.01 mole) in THF (30ml) and
mercapto acetic acid (thioglycolic acid) (0.01 mole) with a pinch of anhydrous
ZnCl$_2$ was refluxed for 12 hours. The solvent was then removed to get a
residue, which was dissolved in benzene and passed through column of silica
gel using benzene: chloroform (8:2; v/v) mixture as eluent. The eluate was
concentrated and the product crystallized from alcohol to give 4-
thiazolidinones (8a-h), which were obtained in 50-60% yield.

The analytical and spectra data of compounds (8a-h) are described.
Schiff base (6 a-h)

\[
\begin{align*}
\text{THF} & \quad \text{Anhydrous} \\
\text{SHCH}_2\text{COOH}
\end{align*}
\]

Where, 4 - Thiazolidinones (8 a - h)

\[
\begin{align*}
\text{Ar} = & \quad 8a = \quad \text{Ph} \\
& 8b = \quad \text{Ph}-\text{OMe} \\
& 8c = \quad \text{Ph}-\text{OH} \\
& 8d = \quad \text{Ph}-\text{OH} \\
& 8e = \quad \text{Ph}-\text{CH}_3 \\
& 8f = \quad \text{Ph}-\text{O} \\
& 8g = \quad \text{Ph}-\text{OH} \\
& 8h = \quad \text{Ph}-\text{OCH}_2\text{CH}_3
\end{align*}
\]
**Compound-8a**

\[
\text{N-(4-(2,4-dichlorophenyl)-6-(6-methynaphthalen-2-yl)pyrimidin-2-yl)-4-(4-o xo-2-phenylthiazolidin-3-yl)benzenesulfonamide}
\]

<table>
<thead>
<tr>
<th>Molecular Formula: ( \text{C}<em>{36}\text{H}</em>{26}\text{Cl}<em>{2}\text{N}</em>{4}\text{O}<em>{3}\text{S}</em>{2} )</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight: 696.09 gm/mole</td>
<td>% C   % H   % N   % S   % Cl</td>
</tr>
<tr>
<td>Melting Point: 186-87°C (Uncorrected)</td>
<td>Calcd  61.98  3.76  8.03  9.19  10.16</td>
</tr>
<tr>
<td>Yield: 60%</td>
<td>Found   61.80  3.71  8.00  9.01  10.04</td>
</tr>
</tbody>
</table>

**Infrared Spectral Features cm\(^{-1}\)**

| 3030, 1600, Aromatic C-H          | PMR spectral Features (\( \delta, \text{ppm} \)) |
| 1500     stretching               | 6.5-7.9 (multiplet,aromatic + H of  |
| 1690     C=O of thiazolidinone    | Pyrimidine ) |

Other band is similar to corresponding Schiff bases.

| 6.44 (H of C\(_2\)H for thiazolidinone) |
| 11.34 (H of SO\(_2\)NH) |

**CMR spectral Features (\( \delta, \text{ppm} \))**

| 114-131 | Benzene |
| 134     | Ar-Cl |
| 163-169 | pyrimidine |
| 171.2   | C = O |
| 33.5    | CH\(_2\) |
| 65.6    | CH |
Compound-8b

N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)-4-(2-(4-methoxyphenyl)-4-oxothiazolidin-3-yl)benzenesulfonamide

**Molecular Formula:** C_{37}H_{28}Cl_{2}N_{4}O_{4}S_{2}

**Molecular Weight:** 726.09 gm/mole

**Melting Point:** 189-90°C (Uncorrected)

**Yield:** 58%

<table>
<thead>
<tr>
<th>Infrared Spectral Features cm⁻¹</th>
<th>PMR spectral Features (δ,ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3030, 1600, stretching</td>
<td>6.5-7.9 (multiplet,aromatic + H of Pyrimidine + H of SO₂NH)</td>
</tr>
<tr>
<td>1500  C=O of thiazolidinone</td>
<td>3.9-4.0 (2H of CH₂ for thiazolidinone)</td>
</tr>
<tr>
<td>1200  Ar-O-CH₃</td>
<td>6.44   (H of C₂H for thiazolidinone)</td>
</tr>
<tr>
<td>Other band is similar to</td>
<td>3.83   (3H, singlet, OCH₃)</td>
</tr>
<tr>
<td>corresponding Schiff bases.</td>
<td>11.34  (H of SO₂NH)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CMR spectral Features (δ,ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>114-131 Benzene</td>
</tr>
<tr>
<td>163-169 pyrimidine</td>
</tr>
<tr>
<td>171.2 C = O</td>
</tr>
<tr>
<td>33.5 CH₂</td>
</tr>
<tr>
<td>158-159 -C – O</td>
</tr>
<tr>
<td>56  CH₃</td>
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**Elemental Analysis**

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<th>%C</th>
<th>%H</th>
<th>%N</th>
<th>%S</th>
<th>%Cl</th>
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</thead>
<tbody>
<tr>
<td>Calcd</td>
<td>61.07</td>
<td>3.88</td>
<td>7.70</td>
<td>8.81</td>
</tr>
<tr>
<td>Found</td>
<td>61.00</td>
<td>3.75</td>
<td>7.62</td>
<td>8.60</td>
</tr>
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</table>

Page 160
Compound-8c

N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)-4-(2-(4-hydroxyphenyl)-4-oxothiazolidin-3-yl)benzenesulfonamide

<table>
<thead>
<tr>
<th>Molecular Formula: C_{36}H_{26}Cl_{2}N_{4}O_{4}S_{2}</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight: 712.19 gm/mole</td>
<td>%C %H %N %S %Cl</td>
</tr>
<tr>
<td>Melting Point: 177-78°C (Uncorrected)</td>
<td>Calcd 60.59 3.67 7.85 8.99 9.94</td>
</tr>
<tr>
<td>Yield: 60%</td>
<td>Found 60.46 3.60 7.80 8.78 9.93</td>
</tr>
</tbody>
</table>

**Infrared Spectral Features cm⁻¹**
- 3030, 1600: Aromatic C-H stretching
- 1500: C=O of thiazolidinone
- 1690: C=O of thiazolidinone (broad)
- 3200-2600: OH phenolic
- 2880, 2920: CH₂
- 1400: Other band is similar to corresponding Schiff bases.

**PMR spectral Features (δ, ppm)**
- 6.5-7.9 (multiplet, aromatic + H of Pyrimidine + H of SO₂NH)
- 3.9-4.0 (2H of CH₂ for thiazolidinone)
- 6.44 (H of C₂H for thiazolidinone)
- 5.35 (H of OH)
- 11.34 (H of SO₂NH)

**CMR spectral Features (δ, ppm)**
- 114-131: Benzene
- 134: Ar-Cl
- 163-169: pyrimidine
- 171.2: C = O
- 33.5: CH₂
- 65.6: CH
**Compound-8d**

![Chemical Structure](image)

N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)-4-(2-(2-hydroxyphenyl)-4-oxothiazolidin-3-yl)benzenesulfonamide

<table>
<thead>
<tr>
<th>Molecular Formula: C_{36}H_{26}Cl_{2}N_{4}O_{4}S_{2}</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight: 712.19 gm/mole</td>
<td>% C  % H  % N  % S  % Cl</td>
</tr>
<tr>
<td>Melting Point: 180-82°C (Uncorrected)</td>
<td>Calcd  60.59  3.67  7.85  8.99  9.94</td>
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<tr>
<td>Yield: 55%</td>
<td>Found  60.48  3.55  7.77  8.79  9.90</td>
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**Infrared Spectral Features cm\(^{-1}\)**

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<th>Frequency</th>
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<tr>
<td>3030, 1600</td>
<td>Aromatic C-H</td>
</tr>
<tr>
<td>1500</td>
<td>stretching</td>
</tr>
<tr>
<td>1690</td>
<td>C=O of thiazolidinone</td>
</tr>
<tr>
<td>3200-2600</td>
<td>-OH phenolic (broad)</td>
</tr>
<tr>
<td>2880, 2920</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>1400</td>
<td></td>
</tr>
</tbody>
</table>

Other band is similar to corresponding Schiff bases.

**PMR spectral Features (\(\delta ppm\))**

<table>
<thead>
<tr>
<th>(\delta ppm)</th>
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<tbody>
<tr>
<td>6.5-7.9</td>
<td>(multiplet,aromatic + H of</td>
</tr>
<tr>
<td></td>
<td>Pyrimidine + H of SO(_2)NH</td>
</tr>
<tr>
<td>3.9-4.0</td>
<td>(2H of CH(_2) for</td>
</tr>
<tr>
<td></td>
<td>thiazolidinone)</td>
</tr>
<tr>
<td>6.44</td>
<td>(H of C(_2)H for</td>
</tr>
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<td></td>
<td>thiazolidinone)</td>
</tr>
<tr>
<td>5.35</td>
<td>(H of OH)</td>
</tr>
<tr>
<td>11.34</td>
<td>(H of SO(_2)NH)</td>
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**CMR spectral Features (\(\delta ppm\))**

<table>
<thead>
<tr>
<th>(\delta ppm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>114-131</td>
<td>Benzene</td>
</tr>
<tr>
<td>134</td>
<td>Ar-Cl</td>
</tr>
<tr>
<td>163-169</td>
<td>pyrimidinene</td>
</tr>
<tr>
<td>171.2</td>
<td>C = O</td>
</tr>
<tr>
<td>33.5</td>
<td>CH(_2)</td>
</tr>
<tr>
<td>65.6</td>
<td>CH</td>
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</tbody>
</table>
Compound-8e

N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)-4-(4-oxo-2-p-tolylthiazolidin-3-yl)benzenesulfonamide

<table>
<thead>
<tr>
<th>MolecularFormula: C_{37}H_{28}Cl_{2}N_{4}O_{3}S_{2}</th>
<th>Elemental Analysis</th>
</tr>
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<tbody>
<tr>
<td>Molecular Weight: 710.10 gm/mole</td>
<td>%C %H %N %S %Cl</td>
</tr>
<tr>
<td>Melting Point: 180-81°C (Uncorrected)</td>
<td>Calcd 62.44 3.97 7.87 9.01 9.96</td>
</tr>
<tr>
<td>Yield: 58%</td>
<td>Found 62.40 3.92 7.83 8.89 9.91</td>
</tr>
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</table>

**Infrared Spectral Features cm⁻¹**
- 3030, 1500, Aromatic C-H
- 1600 stretching
- 1690 C=O of thiazolidinone
- 2880, 2920 -CH₂-
- 1400
- 2950, 1370 -CH₃
- Other band is similar to corresponding Schiff bases.

**PMR spectral Features (δ,ppm)**
- 6.5-7.9 (multiplet, aromatic + H of Pyrimidine + H of SO₂NH)
- 3.9-4.0 (2H of CH₂ for thiazolidinone)
- 6.44 (H of C₂H for thiazolidinone)
- 2.34 (3H, singlet, CH₃)
- 11.34 (H of SO₂NH )

**CMR spectral Features (δ,ppm)**
- 114-131 Benzene
- 134 Ar-Cl
- 163-169 pyrimidine
- 171.2 C = O
- 33.5 CH₂
- 18-21.3 CH₃
**Compound-8f**

![Chemical Structure](image)

4-(2-(benzo[d][1,3]dioxol-5-yl)-4-oxothiazolidin-3-yl)-N-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)benzenesulfonamide

<table>
<thead>
<tr>
<th>MolecularFormula: C_{37}H_{26}Cl_{2}N_{4}O_{5}S_{2}</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight: 740.17 gm/mole</td>
<td>% C</td>
</tr>
<tr>
<td>Melting Point: 189-90°C (Uncorrected)</td>
<td>Calcd 59.92</td>
</tr>
<tr>
<td>Yield: 60%</td>
<td>Found 59.89</td>
</tr>
</tbody>
</table>

**Infrared Spectral Features cm\(^{-1}\)**

- 3030, 1500, 1600: Aromatic C-H
- 1690: C=O of thiazolidinone
- 1200: Ar – O – alkyl
- 2880,2920: - CH\(_2\)
- 1400: Other band is similar to corresponding Schiff bases.

**PMR spectral Features (δ,ppm)**

- 6.5-7.9: (multiplet,aromatic + H of Pyrimidine + H of SO\(_2\)NH)
- 3.9-4.0: (2H of CH\(_2\) for thiazolidinone)
- 6.44: (H of C\(_2\)H for thiazolidinone)
- 6.10: (2H for CH\(_2\) of – O – CH\(_2\) – O-)

**CMR spectral Features (δ,ppm)**

- 114-131: Benzene
- 163-169: pyrimidine
- 171.2: C = O
- 33.5: CH\(_2\)
- 65.6: CH
- 101.2: O – CH\(_2\) – O
**Compound-8g**

N-(4-(2,4-dichlorophenyl)-6-(6-methynaphthalen-2-yl)pyrimidin-2-yl)-4-(2-(4-hydroxy-3-methoxyphenyl)-4-oxothiazolidin-3-yl) benzenesulfonamide

**Molecular Formula:** C$_{37}$H$_{28}$Cl$_2$N$_4$O$_5$S$_2$

**Molecular Weight:** 742.09 gm/mole

**Melting Point:** 190-91°C (Uncorrected)

**Yield:** 58%

**Elemental Analysis**

<table>
<thead>
<tr>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% S</th>
<th>% Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcd</td>
<td>59.76</td>
<td>3.79</td>
<td>7.53</td>
<td>8.62</td>
</tr>
<tr>
<td>Found</td>
<td>59.70</td>
<td>3.73</td>
<td>7.48</td>
<td>8.60</td>
</tr>
</tbody>
</table>

**Infrared Spectral Features cm$^{-1}$**

| 3030, 1600, 1500 1690 | Aromatic C-H stretching C=O of thiazolidinone |
| 3200-2600 1200 2880,2920 1400 | -OH Aryl-alkyl ether - CH$_2$ |

Other band is similar to corresponding Schiff bases.

**PMR spectral Features (δ, ppm)**

- 6.5-7.9 (multiplet, aromatic+H of Pyrimidine + H of SO$_2$NH)
- 3.9-4.0 (2H of CH$_2$ for thiazolidinone)
- 6.44 (H of C$_2$H for thiazolidinone)
- 5.35 (H for OH)
- 3.83 (3H for OCH$_3$)

**CMR spectral Features (δ, ppm)**

- 114-131 Benzene
- 163-169 pyrimidine
- 171.2 C = O
- 33.5 CH$_2$
- 65.6 CH
- 56.1 -OCH$_3$
Compound-8h

NN-(4-(2,4-dichlorophenyl)-6-(6-methylnaphthalen-2-yl)pyrimidin-2-yl)-4-(2-(3,4-diethoxyphenyl)-4-oxothiazolidin-3-yl)benzenesulfonamide

<table>
<thead>
<tr>
<th>MolecularFormula: C_{40}H_{34}Cl_{2}N_{4}O_{5}S_{2}</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight: 784.13 gm/mole</td>
<td>%C  %H  %N  %S  %Cl</td>
</tr>
<tr>
<td>Melting Point: 188-89°C (Uncorrected)</td>
<td>Calcd 61.14 4.36 7.13 8.16 9.02</td>
</tr>
<tr>
<td>Yield: 58%</td>
<td>Found 61.03 4.31 7.10 8.03 9.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Infrared Spectral Features cm(^{-1})</th>
<th>PMR spectral Features (δ,ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3030, 1600, Aromatic C-H</td>
<td>6.5-7.9 (multiplet,aromatic + H of Pyrimidine + H of SO₂NH)</td>
</tr>
<tr>
<td>1500 stretching</td>
<td>3.9-4.0(2H of CH₂ for thiazolidinone)</td>
</tr>
<tr>
<td>1690 C=O of thiazolidinone</td>
<td>6.44 (H of C₂H for thiazolidinone)</td>
</tr>
<tr>
<td>1200 Aryl-alkyl ether</td>
<td>1.32 (6H for 2 CH₃)</td>
</tr>
<tr>
<td>2850, 2920 -CH₂-</td>
<td>4.10 (4H for 2 CH₂)</td>
</tr>
<tr>
<td>1450 Other band is similar to corresponding Schiff bases.</td>
<td><strong>CMR spectral Features (δppm)</strong></td>
</tr>
</tbody>
</table>

| | |
| 114-131 Benzene | |
| 163-169 pyrimidine | |
| 171.2 C = O | |
| 33.5 CH₂ | |
| 65.6 CH | |
Fig. 4.1 IR Spectrum of Compound 8a
Fig. 4.2 IR Spectrum of Compound 8C
Fig. 4.3 IR Spectrum of Compound 8e
Fig. 4.4 NMR Spectrum of Compound 8a
Fig. 4.5 NMR Spectrum of Compound Bb
Fig. 4.6 NMR Spectrum of Compound 8e
Fig. 4.8 CMR Spectrum of Compound 8b
Fig. 4.9 CMR Spectrum of Compound 8e
Fig. 4.10 LC-MS of Compound 8b
4.4 Results and Discussion

Azomethines (6a-h) on cyclo-condensation reaction with thioglycolic acid (mercapto acetic acid) in the presence of anhydrous ZnCl$_2$ yields 4-thiazolidinones (8a-h). Their structures were confirmed by analytical and spectral data. The C, H, N and S contents of the prepared compounds were consistent with their predicted structures as shown in Scheme-4.1. The infrared spectra show the band in the region 1680-1700cm$^{-1}$ for carbonyl group of 4-thiazolidinone ring.

The NMR spectra show a signal at 3.90-4.00 $\delta$ppm for CH$_2$ protons at position-5 in the 4-thiazolidinone ring and a signal at 6.44 $\delta$ for CH protons at position-2 of the 4-thiazolidinone ring. All other signals are at their respective positions for the respective protons in the NMR spectra. The CMR spectrum also show the signal at 171.2 for C = O and 33.5 $\delta$ppm for CH$_2$ of thiazolidinone. All other signals appeared at their respective positions.

The LC-MS spectrum of 8b (Fig. 4.10) indicates that the molecular mass of 8b (i.e. 726) agreed with the peak obtained (726.09).

The analytical and spectral data of the compounds (8a-h) are shown. The IR, NMR and $^{13}$C NMR spectra are scanned in Figures-4.1-4.10 for the selective compounds.
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